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# **Liquid Transport Through Membranes with Mosaic Microdomains: Pervaporation of Ethanol/Water Mixture Through Bisphenol-A-Polycarbonate-Poly(tetramethylene glycol) Multiblock Copolymer Membranes**

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Pervaporation of ethanol/water mixtures at 25°C was examined on (AB)<sub>n</sub> type multiblock copolymer membranes of bisphenol-A polycarbonate (PC) and poly (tetraethylene oxide) (PTMG) with varying PC content (44 to 78%) and block lengths. All the membranes exhibited changes in the permselectivity from ethanol-favoring to water-favoring with increasing ethanol content in the feeds. And the permselectivity for ethanol became smaller with increasing PC content. The best permselectivity was observed for an ethanol-conditioned membrane of 45% PC content toward the mixture of low ethanol content (2 to 5%).

**KEYWORDS:** Membrane Separation / Pervaporation / Separation of Ethanol and Water / Block Copolymer Membrane

## **INTRODUCTION**

In our previous publications<sup>1-3</sup>, we reported swelling and pervaporation behavior of ethanol/water mixtures through multiphase membranes of a randomly coupled bisphenol-A-polycarbonate (PC) and polyoxyethylene (POE) of (AB)<sub>n</sub> type. We coded the samples as BXEY with X and Y being the number-average degrees of polymerization DP of PC and POE blocks, respectively. The BXEY membranes exhibited quite peculiar behavior that we did not anticipate. For example, a membrane from B5E68 (of 25 wt% PC content with relatively long POE blocks) exhibited an extremely high degree of swelling at 25°C in the near azeotropic mixture of 95/5 ethanol/water (v/v) composition rather than in pure water, although POE has a much higher affinity for water than for ethanol. On the other hand, under pervaporation of ethanol/water mixtures at 25°C a membrane from B22E46 (of 75 wt% PC content) exhibited the best performance for dehydrating ethanol from the azeotrope. The BXEY membranes may thus be ranked as a water preferentially-permeating type. Several membranes of a similar potentiality were developed, but only a few were capable of preferential permeation of ethanol.

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In this study we attempted to develop membranes of the latter type. Specifically we examined permeability of ethanol/water mixtures through membranes of multiblock copolymers composed of PC and poly (tetramethylene oxides) (PTMG) of a randomly coupled (AB)<sub>n</sub> type. Again we coded such samples as BXTY with an obvious replacement of POE (E) by PTMG (T). The PTMG segment has higher affinity for ethanol rather than for water, we expected their pervaporation behavior may differ from the BXEY membranes. We discuss the effects of PC/PTMG composition and block lengths of the BXTY membranes on the swelling in and the pervaporation behavior of ethanol/water mixtures.

## EXPERIMENTAL SECTION

### Materials

The copolymer samples were synthesized *via* condensation of bisphenol-A and poly (tetramethylene glycol) (PTMG) prepolymer by the method of Goldberg<sup>5,6</sup>. Commercially available bisphenol-A (Nakarai Chemicals Co. Ltd.) was purified by repeating recrystallization from benzene/methanol (100/5 v/v) mixture, and the obtained white crystalline powder was thoroughly dried under vacuum. For PTMG prepolymer, we used two commercial samples, PTMG-100 and PTMG-500 (Hodogaya Chemicals Co.), of different molecular weight (MW). For purification each PTMG sample was first dissolved in tetrahydrofuran (THF), and then the solution was suspended in excess water. After about 24 h we recovered wax-like PTMG prepolymer floating on the air-water surface. This procedure was repeated twice. Finally the PTMG sample was dried under vacuum at 100°C. The MW and its distribution (MWD) were determined on a gel permeation chromatograph (GPC: Model HLC 801-A, Tosoh Co. Ltd.) with the columns calibrated against polystyrene elution standards (Tosoh Co. Ltd.). The number-average molecular weight  $M_n$  was determined by freezing-point depression using benzene. Table 1 shows the characteristics of the PTMG samples.

Table 1. Characteristics of PTMG prepolymers.

Sample Code	$M_{no}$	$M_{PS}$	$M_w/M_n$	$M_n$
PTMG-100	801-891	3163	1.44	910
PTMG-500	1968-2200	7287	1.72	2100

\*  $M_{no}$  : Nominal molecular weight.

\*\*  $M_{PS}$  : Molecular weight deduced from polystyrene standard.

\*\*\*  $M_n$  : The number average molecular weight determined by freezing point depression method.

The copolymerization was carried out by the method of Goldberg<sup>5,6</sup> *via* the condensation in pyridine of bisphenol-A and PTMG prepolymer of DP=Y with phosgene. The reaction required careful elimination of impurities not only in the monomers but also in the solvent. Thus pyridine was dehydrated by vigorous stirring with CaH<sub>2</sub> for 24 h and then

distilled under pure N<sub>2</sub> stream just before use. Since the polycondensation was an equilibrium reaction, the temperature was kept constant at 27°C as much as possible throughout the reaction.

Table 2 summarizes the recipe for the polycondensation. The prescribed amounts of bisphenol-A and the PTMG prepolymer were dissolved in pyridine. Under rapid and efficient stirring of the mixture kept in a sealed reaction vessel, phosgene purified by bubbling through a series of concentrated sulfuric acid traps was introduced into the mixture. Unreacted phosgene was bubbled into a series of safety traps containing alkali methanol solution to deactivate the gas. The details were describe elsewhere<sup>5,6</sup>.

The block copolymer samples were characterized on the GPC equipped with a built-in refractometer and a ultraviolet (UV) adsorption monitor (the wavelength=254 nm) and also a light-scattering monitor (LALLS: LS-8000, Tosoh Co., Ltd.). The results are summarized in Table 3. The samples were coded as BXTY with X and Y denoting the number average DPs of PC blocks and the PTMG prepolymer, respectively. Strictly speaking, the PTMG block length should be YZ, because occasionally Z pieces of PTMG prepolymer were linked with phosgene instead of PC blocks. However, it turned out Z to

Table 2. Details of the Monomer Feeds in the Polycondensation.

Sample Code	Mole% of Bisphenol-A	Weight of PTMG	Monomer Feed (g) Bisphenol-A
B23T28	50.6	9.4	26.6
B13T11	44.0	9.4	26.6
B15T28	38.6	16.8	19.2
B7T11	36.9	16.8	19.2
B7T28	40.2	22.9	13.1
B6T11	25.4	22.9	13.1

Table 3. Characteristics of BXTY polymers<sup>a)</sup>

Sample Code (BXTY)	Bisphenol A Carbonate Content (wt%)		X	Y	Z	n	M <sub>app</sub> (LALLS-GPC)	M <sub>w</sub> /M <sub>n</sub>
	E.A.	GPC						
B23T28	71.9	72.7	22.8	28	1.05	9.0	$7.20 \times 10^4$	2.66
B13T11	78.5	78.1	12.8	11	1.08	31.3	$1.33 \times 10^5$	1.96
B15T28	62.3	62.7	14.8	28	1.10	19.6	$1.20 \times 10^5$	2.97
B7T11	60.8	63.1	6.7	11	1.17	16.4	$4.59 \times 10^4$	2.52
B7T28	44.1	42.6	7.1	28	1.17	34.6	$1.48 \times 10^5$	1.87
B6T11	56.1	57.6	5.5	11	1.22	26.5	$6.59 \times 10^4$	1.80

be only 1.05 to at most 1.2. Thus we took Y as the representative PTMG block length instead of YZ.

Differential scanning calorimetric (DSC) characterization of the samples was carried out on a DSC (Rigakudenki Model 8055) in the range from 170 to 530 K at a heating rate of 5 K min<sup>-1</sup>.

### Methods

Swelling and pervaporation tests were conducted on the copolymer membranes with 20 to 200  $\mu\text{m}$  thickness either cast from 2 to 5 wt% chloroform solution or compression molded at 220°C under 20 kg/cm<sup>2</sup> for 2 min, degassed for 5 min under 10<sup>-2</sup> atm, and pressed again at 5 kg/cm<sup>2</sup> for 5 min.

For comparison, we prepared homo-PC membranes by the solvent casting from a commercial PC sample (Teijin Co. Ltd., K-1300). Also we prepared homo-PTMG membranes (cr-PTMG) by endcrosslinking PTMG-100 with a tri-functional isocyanate, 2-isocyanatoethyl 2,6-diisocyanato-hexanoate (Toray Ind. Inc., T-100). The mixture was kept at 120°C for 10 min in a molding cell, and compression molded at 20 kg cm<sup>-2</sup> *in situ* for 2 h. Then, the films were aged for one week before use. The details of the swelling and pervaporation experiments were described elsewhere<sup>1-4,6</sup>.

### Principles

The equilibrium degree of swelling  $q_e$  (g-sorbed liquid/100 g-membrane) was determined by weighing method<sup>1-4,6</sup>. The pervaporation data were analyzed according to Aptel *et al*.<sup>7</sup>

$$P = DS_e = D\kappa q_e \quad (1)$$

$$\kappa^{-1} = (q_e/d_s) + (100/d_m) \quad (2)$$

where  $P$  (g cm<sup>-1</sup> s<sup>-1</sup>) is the rate of pervaporation;  $D$  (cm<sup>2</sup> s<sup>-1</sup>), the concentration-dependent average diffusion rate;  $S_e$  (g-liquid/cm<sup>3</sup>-membrane), the solubility of the permeating liquid to the membrane; and  $\kappa$ , the reduction factor defined by eq 2. We estimated  $S_e = \kappa q_e$  from the  $q_e$  data using eq 2 with the densities  $d_s$  and  $d_m$  of the sorbed liquid and the membrane, respectively.

The selective permeation from a binary mixture A/B can be conveniently expressed in terms of the separation factor  $\alpha_A$  (or  $\alpha_B$ ) defined as:

$$\alpha_A = (Y_A/Y_B)/(X_A/X_B) = 1/\alpha_B \quad (3)$$

where  $X_K$  and  $Y_K$  are the weight fractions of the species K (K=A or B) in the feed and in the permeate, respectively<sup>8</sup>. If  $\alpha_A < 1$ , the preferentially permeating species is B.

If the liquids A and B permeate independently, the pervaporation rate  $P_K^{\text{id}}$  of the component K should be given by<sup>8</sup>

$$P_K^{\text{id}} = X_K P_K^\circ \quad (K=A \text{ or } B) \quad (4)$$

where  $P_K^\circ$  is the observed pervaporation rate of the pure liquid K. Since the ideal pervaporation implicitly assumes an additivity of the fluxes, the total ideal rate  $P^{\text{id}}$  should be

$$P^{id} = P_A^{id} + P_B^{id} = X_A P_A^\circ + X_B P_B^\circ \quad (5)$$

Huang *et al.*<sup>9,10</sup> introduced permeation ratios  $\theta$  and  $\theta_K^{obs}$  as a measure of the deviation of the observed rates  $P$  and  $P_K^{obs}$  from the ideal rates  $P^{id}$  and  $P_K^{id}$ , respectively

$$\theta = P/P^{id} \quad (6)$$

$$\theta_K = P_K^{obs}/P_K^{id} = P/X_K P_K^\circ \quad (K=A \text{ of } B) \quad (7)$$

where  $P_K^{obs} = Y_K P$  is the observed pervaporation rate of the component  $K$ . The parameters defined by eqs 6 and 7 reflect the liquid/liquid interactions in the membrane.

For achieving efficient separation of the component  $K$  in the A/B mixture, the membrane should have a high value of the separation factor  $\alpha_K$ . However, if the high  $\alpha_K$  membrane has a low value of  $P_K$ , the membrane is not quite efficient, because the permeation rate  $P$  is small. However, the flux  $J$  ( $\text{g cm}^{-2} \text{s}^{-1}$ ) that is the amount of the mixture passed through unit area of the membrane per unit time is given by  $J = P/\ell$  with  $\ell$  being the membrane thickness. The drawbacks due to the slow permeation (small  $P$ ) can be compensated by designing a module with a thin and large-area membrane so that the flux  $J$  can be large. In general, the flux  $J$  is often inversely related to  $\alpha$ , thus the factor  $J\alpha$  is a good measure in representing the total membrane performance<sup>11</sup>.

## RESULTS

### Behavior in pure liquids

Figures 1a and 1b show equilibrium degrees of swelling  $q_e$  at 25°C of the membranes examined in water and ethanol, respectively. Since ethanol is a good solvent but water, a nonsolvent to PTMG, the  $q_e$  is large in ethanol but virtually zero in water. The PC membrane is barely swellable in ethanol but hardly swellable in water. Thus, all BXTY membranes did not swell in water but swelled 20 to 50% in ethanol. B15T28 with 60% PC content showed the largest  $q_e$  among the samples tested. However, the  $q_e$  of BXTY was generally much smaller in both water and ethanol than BXEY<sup>2</sup>.

Figures 1a and 1b also show pervaporation rates  $P$  at 25°C of water and ethanol, respectively, for all the membranes tested. The rates of water  $P_{\text{WATER}}^\circ$  are virtually the same, but the rates of ethanol  $P_{\text{EtOH}}^\circ$  show a clear dependence on PC/PTMG composition. The rate  $P_{\text{EtOH}}^\circ$  is large for the membranes with 60% PC content and especially short blocks. It appears that the dependence of  $P$  on the block length reflects difference in the microphase separated structures. The BXTY polymers especially of short blocks must have diffuse interphase that facilitate the permeability for small molecules.

Comparing Figures 1a and 1b, we see that the  $P_{\text{EtOH}}^\circ$  is higher than  $P_{\text{WATER}}^\circ$  for all the membranes. Especially for B6T11 the former is about 10 times larger than the latter.

From these  $q_e$  and  $P$  ( $P_K^\circ$ ) data for the pure liquids we can estimate the average diffusion rate  $D_K^\circ$  with eq 1. The  $D_{\text{WATER}}^\circ$  was hardly affected by the PC content, but the  $D_{\text{EtOH}}^\circ$  showed a strong dependence on the PC content as well as on the block length. The latter was of the same level or rather smaller than the former, as opposed to the be-

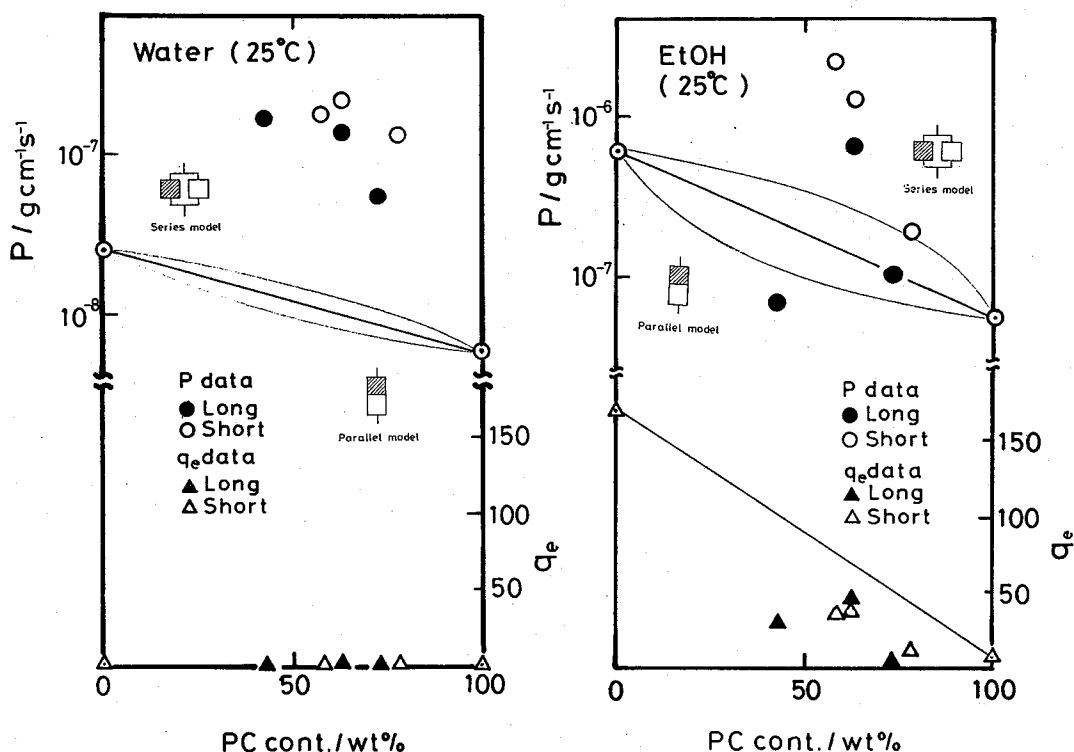


Fig. 1. Pervaporation rates  $P$  ( $\text{g cm}^{-1} \text{s}^{-1}$ ) and equilibrium degrees of swelling  $q^e$  (g liquid/100 g dry membrane) at 25°C as a function of PC content of the membranes examined for water (left) and ethanol (right) at 25°C. The results of  $P$  calculated by the mixture rules are shown with thin lines.

havior of the pervaporation rate  $P_K^0$ . These results imply that the permeability of ethanol depends on the solubility, while the permeability of water is governed by the diffusivity. This trend is opposite to that of BXEY membranes<sup>2</sup> in which the permeability of water is governed by the solubility but that of ethanol, by the diffusivity. The B7T28 membrane having the smallest PC content and long PTMG block shows low  $P_{\text{EtOH}}^0$  and  $D_{\text{EtOH}}^0$ . These facts seem to be due to the existence of the crystalline phase.

Figure 2 shows DSC thermograms of all BXTY and cr-PTMG samples. Exothermic peaks observed in BXTY at about 400 to 500 K range reflect recrystallization of PC segments. For cr-PTMG an endothermic peak is observed at 303 K for the melting of PTMG crystallites. Also for B7T28 a PTMG crystallization peak is observed at around 298 K, but all other BXTY samples do not show this peak. These results suggest that neither the PTMG nor PC crystalline phase exist in these membranes except B7T28 and cr-PTMG at 298 K, where the pervaporization experiments were conducted. However, at the downstream surface of the membranes extensive vaporization of the permeates took place and the surface temperature was found to be as low as 283 to 293 K due to the loss of the enthalpy of vaporization of the permeating liquid. Thus, PTMG crystallites may develop dur-

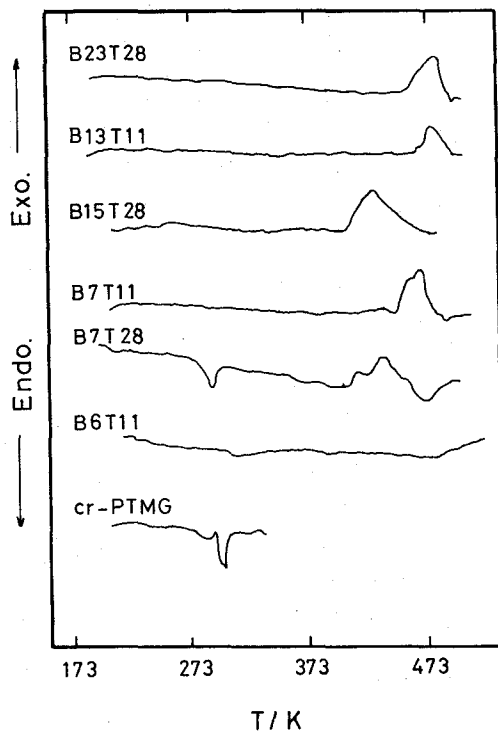


Fig. 2. DSC thermograms of cr-PTMG and BXTY membranes.

ing the pervaporization experiment and disturb the permeation of the liquid, at least, in B7T28 and cr-PTMG membranes.

#### Separation of ethanol/water mixtures

Figures 3a to 3d show the equilibrium degrees of swelling  $q_e$  at 25°C *versus* the ethanol content  $X_{EtOH}$  in ethanol/water mixtures for as-cast PC and cr-PTMG membranes (top-left), two samples of about 75% PC content (top-right), those of 60% PC content (bottom-left) and that (B7T28) of 40% PC content (bottom-right).

All the BXTY samples swell better in ethanol than in water. The general trend is that the  $q_e$  increases with increasing  $X_{EtOH}$  to a maximum swelling at about  $X_{EtOH}=80\%$ . Particularly B13T11, B15T28 and B7T28 exhibit a rather sharp maximum, which is similar to that of cr-PTMG. However, comparing Figure 3a and 3d, we notice that the maximum  $q_e$  of BXTY samples are by a factor of 10 smaller than that of cr-PTMG. These results imply that the affinity of PTMG segments to ethanol was reduced by the block copolymerization with PC segments. Another feature is that B7T11 and B6T11 swell to some extent in the mixtures of  $X_{EtOH}$  less than 50%. We also notice that the  $q_e$  decreases with increasing PC content of the samples. The  $q_e$  is particularly low for B13T11 and B23T28 with 75% PC content.

We now examine the permselectivity of as-cast BXTY membranes for the pervaporation of ethanol/water mixtures. Figure 4a to 4d show the ethanol content  $Y_{EtOH}$  in the



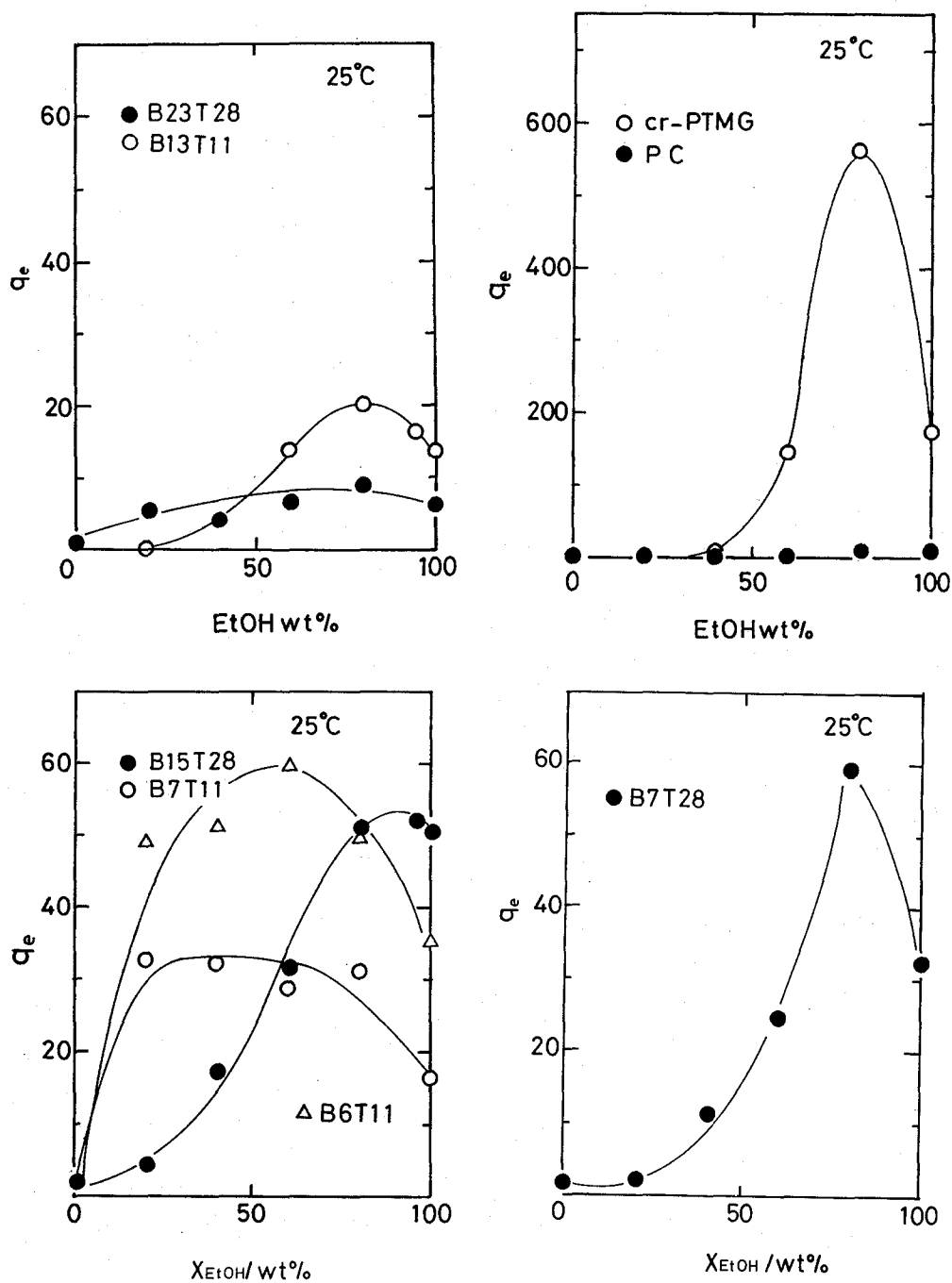


Fig. 3. Equilibrium degrees of swelling  $q_e$  of PC and cr-PTMG (top-left); two BXTY membranes of about 75 wt% PC content (top-right); three BXTY membranes of about 60 wt% PC content (bottom-left); and one BXTY membrane of 40 wt% PC content (bottom-right) in ethanol/water mixtures at 25°C. For the sample codes, see Table 3.

permeated mixture and the separation factor  $\alpha_{\text{EtOH}}$  versus the ethanol content  $X_{\text{EtOH}}$  in the feed mixture for the four BXTY membranes. The dotted curve indicates the vapor composition curve derived from the liquid vapor phase equilibrium of ethanol/water mixtures at 25°C<sup>12</sup>.

For B7T11 and B15T28 membranes, the ethanol contents  $X_{\text{EtOH}}$  in the feeds and  $Y_{\text{EtOH}}$  in the permeates are nearly equal except for the mixture of  $X_{\text{EtOH}}$  about 10%, for which the  $\alpha_{\text{EtOH}}$  is about 2. And the  $\alpha_{\text{EtOH}}$  decreases to 1 with increasing  $X_{\text{EtOH}}$  from 10% to 90%. The tendency is the same for B13T11 membrane. The values of  $Y_{\text{EtOH}}$  are much lower than that expected from the phase equilibrium curve at 25°C of the EtOH/water mixtures, implying that the as-cast membranes unexpectedly suppress the permeation of ethanol, except for the mixtures of very low  $X_{\text{EtOH}}$ .

For an as-cast B7T28 membrane of 45% PC content and long blocks shown (open circles), the ethanol content  $Y_{\text{EtOH}}$  of the permeate becomes lower than  $X_{\text{EtOH}}$  for the mixtures of high  $X_{\text{EtOH}}$  especially of the near azeotropic composition (95.5% at 25°C). In fact, the separation factor  $\alpha_{\text{EtOH}}$  becomes as low as 0.35 for the azeotrope, implying that the water is the preferentially permeating component. For this membrane the preferentially permeating component changes from ethanol to water with increasing  $X_{\text{EtOH}}$  beyond 80%.

Figure 4 also shows results of pervaporation through an ethanol-conditioned B7T28 membrane (closed circles) which clearly exhibits a tendency of preferential permeation of ethanol for the mixtures of  $X_{\text{EtOH}}$  less than 10%. The  $\alpha_{\text{EtOH}}$  is as high as 13 for the mixture of  $X_{\text{EtOH}}=2\%$ , and decreases rapidly with increasing  $X_{\text{EtOH}}$ . Among all the BXTY membranes tested the ethanol-conditioned B7T28 membrane is the best in extracting ethanol from the mixture of low  $X_{\text{EtOH}}$  if compared for the permselectivity.

Now we turn our attention to the prevaporation rates  $P$  of the ethanol/water mixtures through these membranes. The rates  $P$  vary from one membrane to another and from one mixture to another.

Figure 5 shows plots of the rates  $P$  (open circles) together with the equilibrium degrees of swelling  $q_e$  (closed triangles) at 25°C versus the ethanol content in the feed  $X_{\text{EtOH}}$  for the as-cast membranes. The figure for B7T28 includes the data for the ethanol-conditioned membrane (closed circles). The dotted curves show the ideal pervaporation rates  $P^{\text{id}}$  estimated with eq 5 from the data for the pure liquids shown in Figures 1.

For B7T11 and B13T11 the observed rates  $P$  are much lower than the ideal rates  $P^{\text{id}}$  for the mixtures of any composition, except one example. For these systems the  $\alpha_{\text{EtOH}}$  was only 2 to 1. The behavior of B15T28 is peculiar. The observed rates  $P$  agree with the ideal rates  $P^{\text{id}}$ , complying with the results that the  $\alpha_{\text{EtOH}}$  is almost 1 and the permselectivity is completely absent.

On the other hand, only the as-cast B7T28 membrane exhibits an accelerated pervaporation. The observed rates  $P$  are larger by a factor of 2 to 6 than the ideal rates  $P^{\text{id}}$ . Corresponding to the change in  $\alpha_{\text{EtOH}}$  from the ethanol preferential-type ( $>1$ ) to the water preferential-type ( $<1$ ), we see that the rate  $P$  slowly decreases with increasing  $X_{\text{EtOH}}$  up to 50%, but increases again beyond 50%  $X_{\text{EtOH}}$ . For the 50% mixture the rate  $P$  approaches to  $P^{\text{id}}$ , where  $\alpha_{\text{EtOH}}$  becomes 1 (cf., Figure 4).

For the ethanol-conditioned B7T28 membrane, the  $\alpha_{\text{EtOH}}$  was as high as 13 for the low  $X_{\text{EtOH}}$  mixture. However, for this membrane the rate  $P$  of ethanol is much smaller than

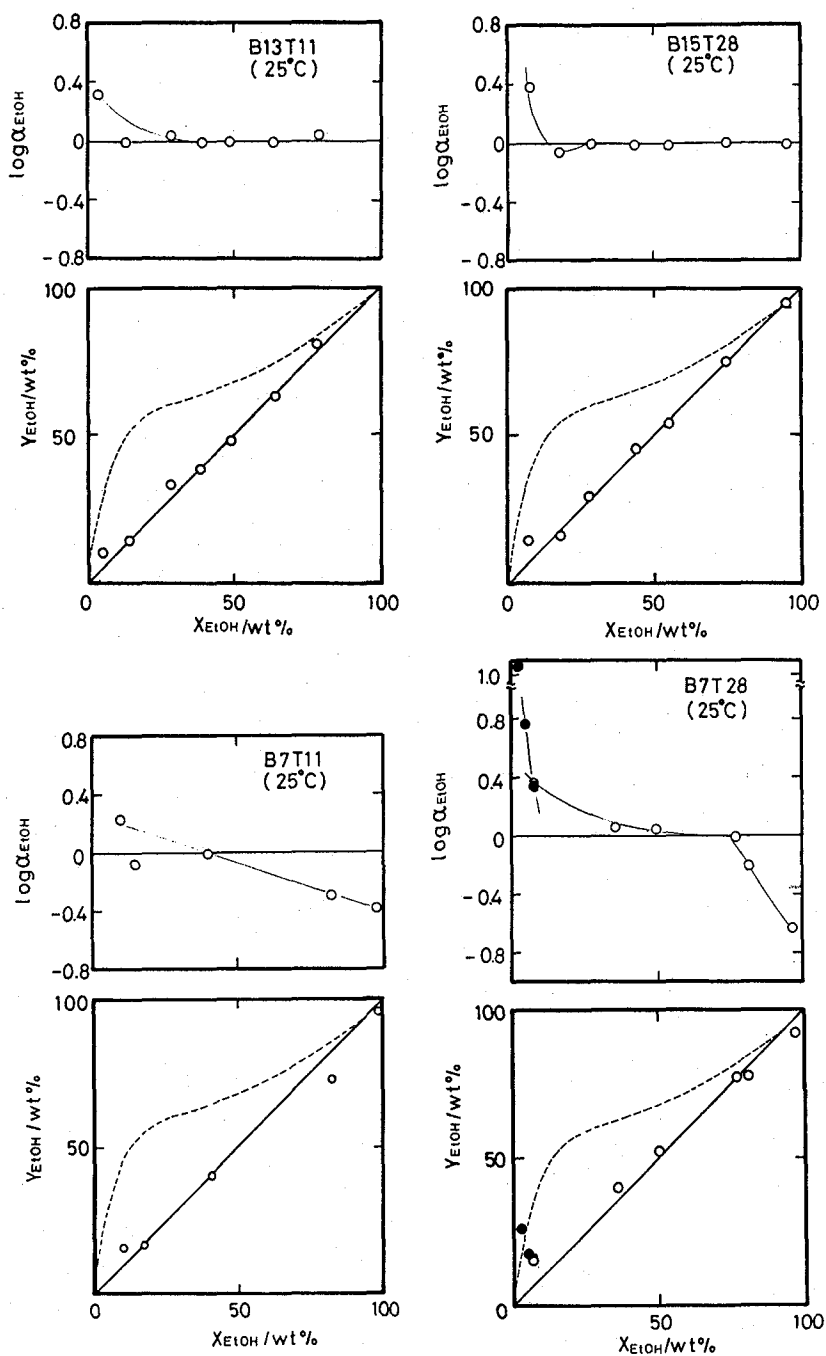


Fig. 4. Ethanol composition  $Y_{EtOH}$  in the permeates and the separation factor  $\alpha_{EtOH}$  as a function of ethanol composition  $X_{EtOH}$  in the feeds for pervaporation of ethanol/water mixtures at 25°C through B13T11 (top-left); B15T28 (top-right); B13T11 (bottom-left); and B7T28 as-cast (open circles) and ethanol-conditioned (closed circles) membranes (bottom-right).

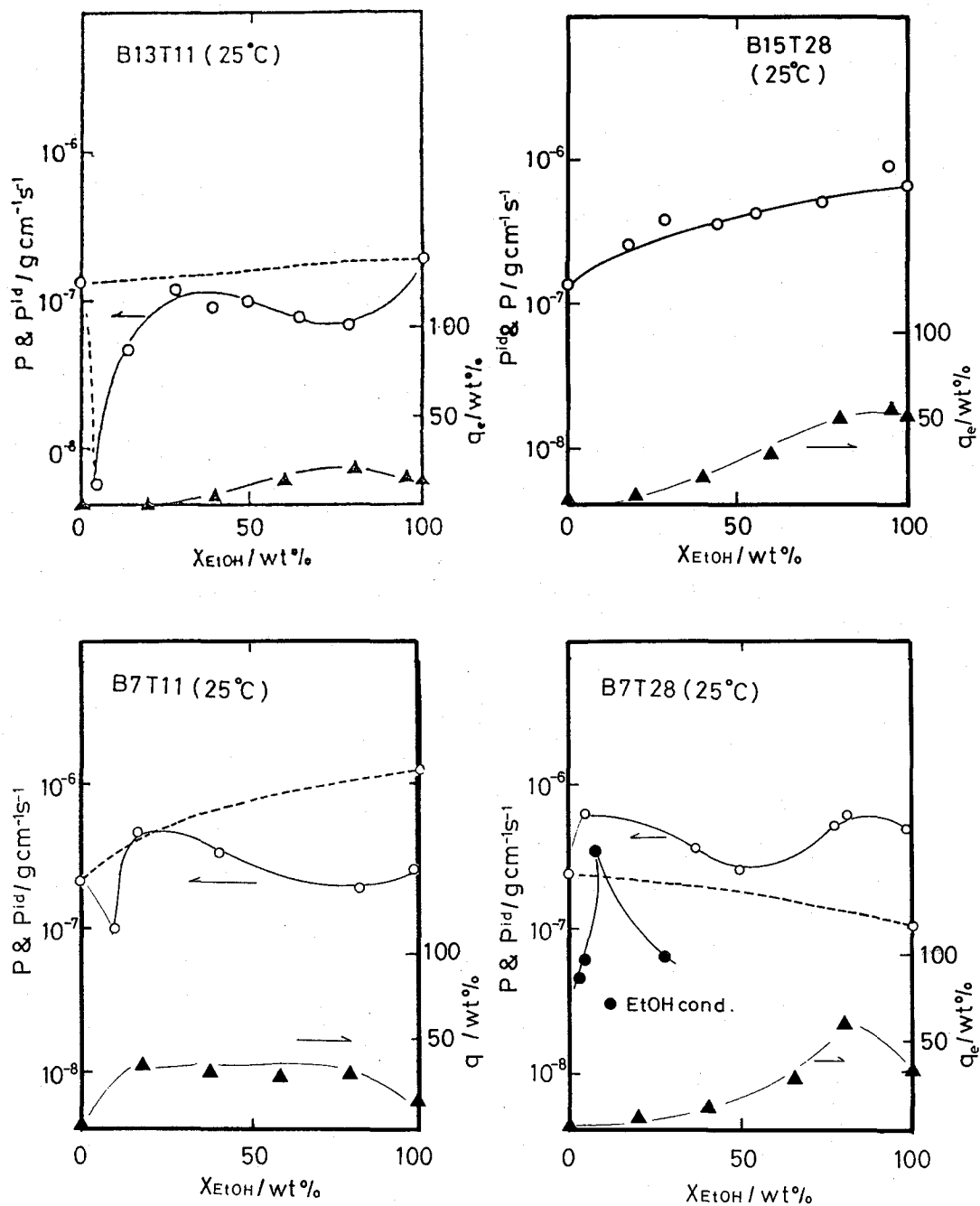


Fig. 5. Observed  $P$  (open circles) and ideal  $P^{id}$  (dotted curves) pervaporation rates as a function of ethanol composition  $X_{EtOH}$  in the feeds for pervaporation at 25°C through B13T11 (top-left), B15T28 (top-right), B7T11 (bottom-left) and B7T28 (bottom-right). Equilibrium degrees of swelling  $q_e$  are also shown (closed triangles).

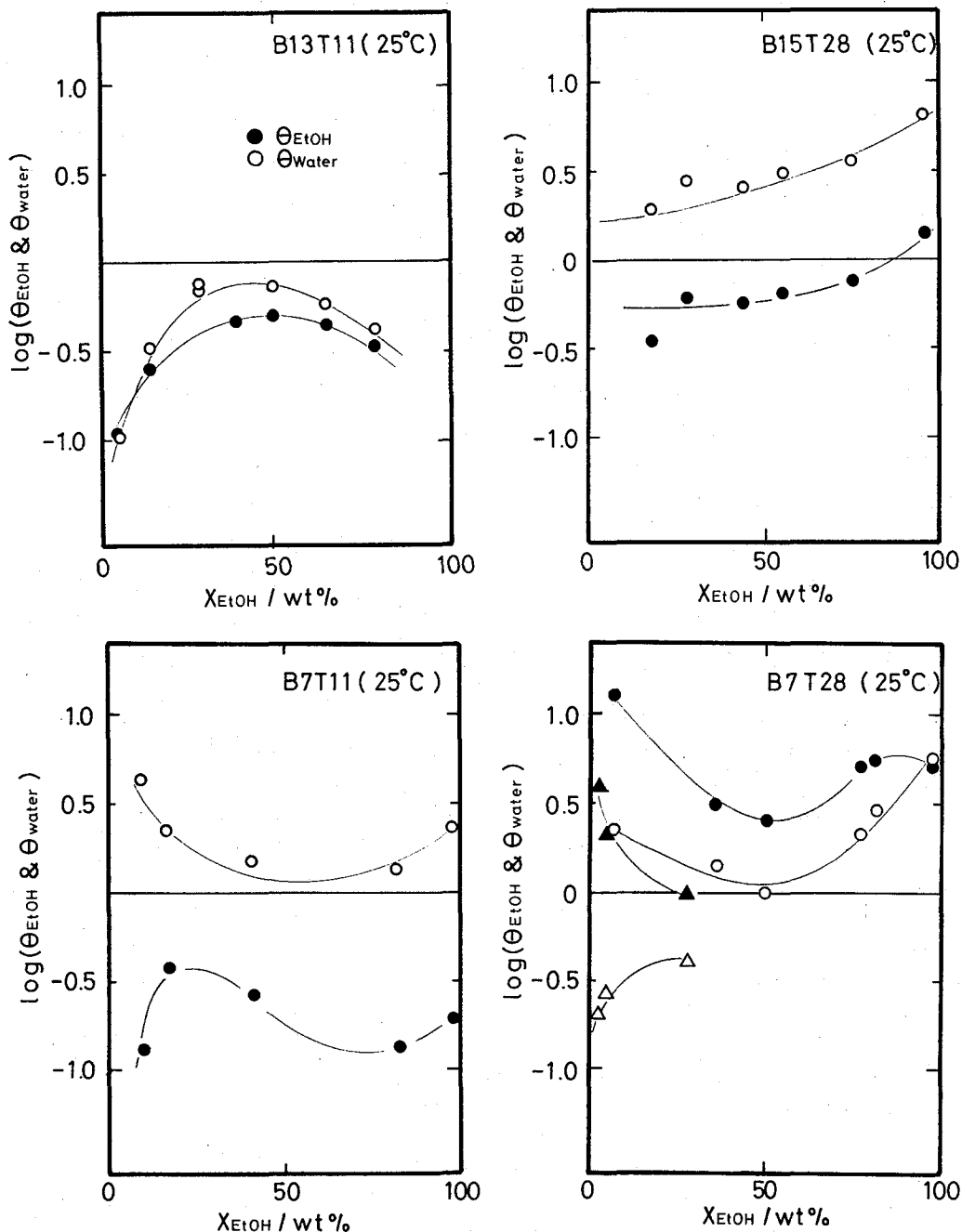


Fig. 6. Plots of  $\log$  (permeation ratio  $\theta_{water}$ ) (open circles) and  $\log$  ( $\theta_{EtOH}$ ) (closed circles) as a function of ethanol composition  $X_{EtOH}$  in the feeds for pervaporation at 25°C through B13T11 (top-left), B15T28 (top-right), B7T11 (bottom-left) and B7T28 (bottom-right). Equilibrium degrees of swelling  $q_e$  are also shown (open and closed triangles).

the ideal rate  $P^{id}$ . Again, unfortunately, the membrane having a high permselectivity possesses only a low permeability.

Finally we examine the permeation ratio  $\theta_K$  [ $K$ =EtOH (solid circles) or WATER (open circles)] defined by eq 6. Figure 6 summarizes the results. For B13T11 the  $\theta_K < 1$  for both EtOH and water, while for B7T11 and B15T28 the  $\theta_{EtOH} < 1$  but  $\theta_{WATER} > 1$ . Interestingly the overall  $\theta = P/P^{id}$  for B15T28 is nearly 1 for the mixtures of any  $X_{EtOH}$  (cf., Figure 5 top-left). For the as-cast B7T28 membrane,  $\theta_K > 1$  for both EtOH and water. For the ethanol-conditioned B7T28, however, the  $\theta_{EtOH} > 1$  and the  $\theta_{WATER} > 1$ . And the  $\theta_{EtOH}$  rapidly decreases, while  $\theta_{WATER}$  increases with increasing  $X_{EtOH}$  in the feed.

## DISCUSSION

Separation of mixtures of two liquids A and B such as ethanol and water that have a high mutual affinity is an intriguing but a complex problem. Even when we employ a membrane material highly selective toward one of the liquids, say A, the strong affinity of A to B induces take-up of B into the membrane swollen with A. Thus the permselectivity is often hampered. This appears to be the case in the pervaporation of ethanol/water mixtures through BXTY membranes of which the permselectivity was rather low. Some BXTY membranes showed preferential permeation of ethanol, but the overall performance was usually not quite satisfactory to meet our requirement of developing an efficient membrane system for ethanol from dilute aqueous solutions such as usually encounter in biomass technology.

However, several findings in this study are interesting and worthy of note. For the BXTY membranes the permselectivity changes from ethanol-favoring to water-favoring with increasing  $X_{EtOH}$  in the feeds. Comparing the membranes of different PC/PTMG content, we notice that the permselectivity for ethanol becomes large with decreasing PC content. In most of the cases, however, the permeation ratio  $\theta_{EtOH}$  is smaller than  $\theta_{WATER}$ , and the separation factor  $\alpha_{EtOH}$  is usually close to 1. The ethanol content  $Y_{EtOH}$  in the permeate is almost always lower than that expected from the liquid-vapor phase equilibrium curve of the ethanol/water mixtures.

Exception to such behavior was found only in a few cases, typically in the ethanol-conditioned B7T28 membrane that showed the separation factor  $\alpha_{EtOH}$  of 10 to 13, although this high selectivity was limited only for very low  $X_{EtOH}$  (2 to 5%) mixtures. Unfortunately, however, the pervaporation rate of such membranes was usually low. The high affinity of ethanol to PTMG segments results in the high selectivity but, at the same time, results in the retardation of the permeation of ethanol.

Another possible reason for the low permeability of the B7T28 membrane might be due to the existence of the PTMG crystalline phase. In the six BXTY membranes examined by DSC, only this sample exhibited an endothermic peak due to the melting of PTMG crystallites. Although one might think its existence is rather unlikely especially in the swollen membrane, the PTMG crystalline phase may exist, because the down stream surface of the membrane is constantly evacuated and is deprived of the enthalpy of vaporization, thus its temperature being low. In general the crystalline phase acts as the tortuous factor and decreases the permeability<sup>13</sup>.

The low permeation rate of a high-selectivity membrane appears to be a general tendency encountered in membrane separation of liquid mixtures. This is particularly true for the case in which the liquid components have a strong mutual affinity. Selective solvation of the membrane with one of the permeates does not help this situation. Separation of ethanol/water mixtures with BXTY membranes is also the case. Of course we can compensate this deficiency by designing a module for separation with a very thin and large-area membrane, if such a membrane has sufficient strength.

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